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SUBJECT: PRELIMINARY RESULTS OF SURFACE WATER MONITORED FOR FORESTRY HERBICIDES IN THE YUROK ABORIGINAL TERRITORY IN THE KLAMATH RIVER WATERSHED, SPRING 1999

SCOPE OF THIS MEMORANDUM

The purpose of this memorandum is to provide results of water sampling conducted in the Klamath River watershed by the Department of Pesticide Regulation (DPR). This study was initiated, in conjunction with the U.S. Environmental Protection Agency and the Yurok Tribe, to address tribal concerns about the potential presence of herbicide residues in surface water. Tribal people live near land owned by a timber company that uses herbicides for forestry management. Data included here are from the period April 20, 1999 to May 15, 1999, with results of chemical analyses. This memorandum summarizes the first sampling results of a three-year study, initiated in 1998, designed to monitor the occurrence of forestry herbicides, atrazine, triclopyr, and 2,4-D, in selected creeks of the Klamath River watershed. Future memoranda will also include chemical results for additional applications and herbicides. An in-depth interpretation of the data is not included here but will be provided in the final report, which will include data from all three years of the study.

Sample and Data Collection

On May 2, 1999, samples were collected at two tributaries and one creek near the ground application sites. On May 14, 1999, samples were collected at one creek near the aerial application sites (Table 1, Table 2, and Figure 1). Rain runoff occurred on each of the sampling dates, and samples were taken after the water level was increased by the runoff.

Table 1. Herbicide application descriptions at sampling sites in Del Norte and Humboldt Counties.

Site	Description	Application type	Application date	Application time	Acres treated	Total AI used (lb)	Application slope (%)[a]	Intermediate slope (%)[b]
A	Terwer Creek Tributary	Ground	4/20/99	1100	9	32 lb. atrazine	40	31
B	Blue Creek	Ground	4/21/99	1700	36	130 lb. atrazine & 20 lb. triclopyr	33	3
C	Pecwan Creek Tributary	Ground	4/26/99	1400	25	91 lb. atrazine	27	3
D	Terwer Creek	Aerial	5/5/99	1000	360	360 lb. triclopyr & 338 lb. 2,4-D	34	8

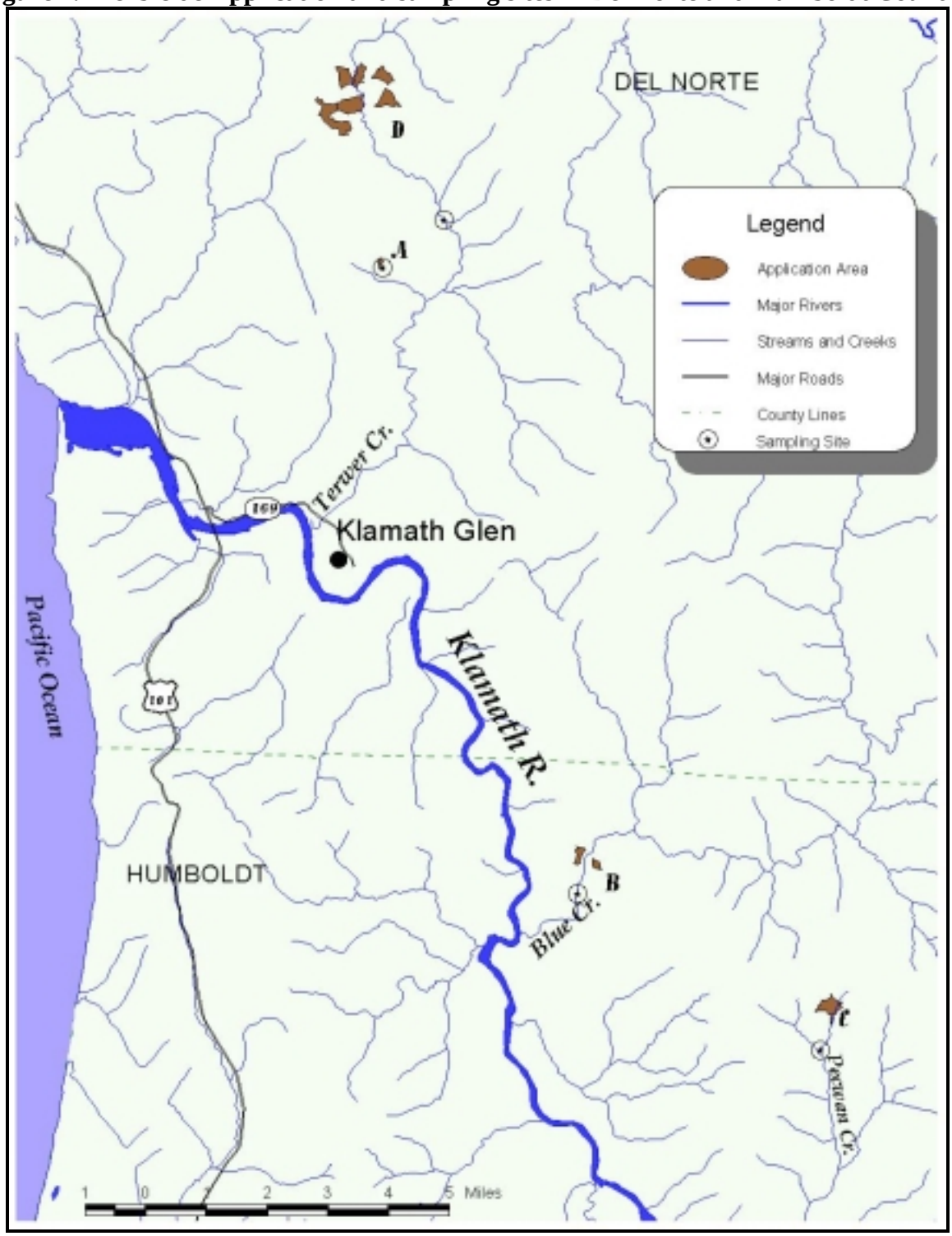
a=change in elevation from top to bottom of application site (ft)/distance (ft) X 100
b=change in elevation from bottom of application to sampling site (ft)/distance (ft) X 100
Elevation and distance estimated on USGS 7.5 minute Quad maps

Table 2. Sampling site descriptions in Del Norte and Humboldt Counties.

Site	Description	Coordinates	Elevation*	Distance from application site	Precipitation (inches)[a]
A	Terwer Creek Tributary	N 41^0 35' 1.5", W 123^0 58' 53.9"	1255 ft.	80 feet	0.08
B	Blue Creek	N 41^0 26' 5.7", W 123^0 54' 38.8"	86.4 ft.	.5 miles	1.12
C	Pecwan Creek Tributary	N 41^0 23' 55.4", W 123^0 49' 58.2"	2326 ft.	.5 miles	1.32
D	Terwer Creek	N 41^0 35' 37.6", W 123^0 57' 42.9"	556 ft.	2.0 miles	0.64

* Elevation data from TrimbleNavigation GeoExplorer I GPS
a=total precipitation from application date to sampling date, gauged at the Turwar Creek station operated by DWR and USGS. Location = 41.5120^0 N, 123.999^0 W, Elevation 6 ft.

Figure 1. Herbicide Application and sampling sites in Del Norte and Humboldt Counties



All water samples were collected as a grab sample from the main flow of the creek, using an ISCO® automatic sampler. Samples were taken at four time-intervals for each site. In addition, herbicide samples were collected from the mixture in the spray tank to be applied at each site. All samples were stored on wet ice or in a 4^0C refrigerator until analysis.

Environmental Measurements

Water quality parameters measured *in situ* included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO). Water pH was measured using a Sentron® (model 1001) pH meter. Water temperature and EC were measured using an Orion® conductivity-salinity meter (model 140). DO was measured using an YSI® dissolved oxygen meter (model 58).

Herbicide Analyses

Herbicide analyses of water samples were performed by the CDFA Center for Analytical Chemistry. Atrazine, a triazine herbicide, was analyzed using high performance liquid chromatography (HPLC) with an ultraviolet (UV) detector, and gas chromatography (GC) with a nitrogen phosphorus detector (NPD). The phenoxy herbicides, 2,4-D and triclopyr, were analyzed by GC on a capillary column using a mass selective detector (MSD). The reporting limit (reliable detection level) for atrazine is 0.05 parts per billion (ppb), and 0.10 ppb for 2,4-D and triclopyr.

RESULTS

Herbicide Concentrations

Table 3 shows chemical analysis results. Four tank samples were analyzed for the percentage of chemical mixed in each application batch. The tank samples for Sites A and C contained 2.37% and 2.93% atrazine, respectively. The tank sample for Site B contained 2.28% atrazine and 0.26% triclopyr, and the tank sample for Site D contained 1.27% triclopyr and 1.13% 2,4-D. According to the label guidelines for forestry management application rates, the maximum allowable are: Atrazine-ground, 4%; triclopyr-ground, 4.4%; triclopyr-aerial, 2.2%; 2,4-D-aerial, 2.5%. All applications were made within the label rates. There were no detections of any of the herbicides in the surface water samples.

Table 3. Concentrations of herbicides in spray tank and surface water samples.

Date	Time	Sample type	Site	Atrazine	Triclopyr	2,4-D
4/20/99	8:50	Tank	A	2.37%	--	--
4/21/99	10:31	Tank	B	2.28%	0.26%	--
4/26/99	10:45	Tank	C	2.93%	--	--
5/4/99	15:45	Tank	D	--[a]	1.27%	1.13%
5/1/99	19:13	Water	A	ND[b]	--	--
	19:36	Water	A	ND	--	--
	20:36	Water	A	ND	--	--
	21:36	Water	A	ND	--	--
5/2/99	11:22	Water	B	ND	ND	--
	12:22	Water	B	ND	ND	--
	13:22	Water	B	ND	ND	--
	14:22	Water	B	ND	ND	--
	10:02	Water	C	ND	--	--
	11:02	Water	C	ND	--	--
	12:02	Water	C	ND	--	--
	13:02	Water	C	ND	--	--
5/14/99	9:16	Water	D	ND	ND	ND
	12:10	Water	D	ND	ND	ND

a=herbicide not used and hence not analyzed
b=ND-none detected at the reporting limit for that chemical.
Minimum Reporting Limit: atrazine = 0.05 ppb, triclopyr and 2,4-D = 0.1 ppb

Environmental Measurements

Table 4 presents the data for pH, DO, temperature, and EC. Water temperature ranged from 7.3 to 9.5^0C, DO ranged from 10.88 to 11.33 mg/L, and pH values ranged from 6.9 to 7.7. EC was taken at a single site and was recorded at 58.7 : S/cm. The California Regional Water Quality Control Board (CRWQCB) (1994), lists the following water quality guidelines as acceptable for the Lower Klamath River hydrologic area (HA): DO above 8.0 mg/L, pH between 6.5 and 8.5, and EC below 200 : S/cm 90% of the time (90% Upper Limit) and below 125 : S/cm 50% of the time (50% Upper Limit). The plans do not provide an acceptable range for temperature, but the Lower Klamath River HA is designated as cold interstate water and its natural receiving water temperature shall not be altered. All water quality measurements taken fall within the CRWQCB's acceptable guidelines.

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Table 4. Water quality measurement at sampling sites.

Date	Site	Temperature (^{0} C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (μS/cm)
5/2/99	Terwer Creek Tributary	9.3	7.5	10.88	*
5/2/99	Blue Creek	8.8	7.7	11.06	*
5/2/99	Pecwan Creek Tributary	7.3	6.9	10.99	*
5/14/99	Terwer Creek	9.5	7.6	11.23	58.7

* Unable to take reading due to drained battery

References

The California Regional Quality Control Board. 1994. Water Quality Control Plan, Region 1, North Coast Region. Santa Rosa, California.